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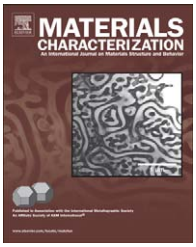

Thermoelectric properties of Cu-added Zn–Sb based alloys with multi-phase equilibrium

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ABSTRACT

The polycrystalline samples of Cu-added Zn–Sb based alloys with multi-phase equilibrium were prepared by spark plasma sintering and their microstructures and thermoelectric properties were evaluated. After Cu addition into Zn–Sb based alloys we observed a major phase ZnSb, β-Zn_4Sb_3, the second phase Cu_2Sb and remnant Zn. The ZnSb phase plays an important role in increasing Seebeck coefficient (α) and decreasing electrical conductivity (σ), and Cu_2Sb is of significance to the improvement of the thermoelectric performance. The thermal conductivities (κ) increase with Cu content, and are almost independent of temperature below 574 K. If in comparison with the highest *ZT* value (*ZT* = 0.48, at 654 K) of Zn_4Sb_3 prepared in the present work, we obtain the value of 0.7 for the alloy with a certain Cu concentration at the corresponding temperature.

1. Introduction

β-Zn_4Sb_3, one of the stable compounds used in intermediate temperatures, has attracted a lot of interest as a thermoelectric material due to its low lattice thermal conductivity. However, since the evaporation of element Zn during sintering, pure β-Zn_4Sb_3 phase cannot easily be obtained, and multi-phase structures, which include β-Zn_4Sb_3, ZnSb and remnant Zn, are usually observed [1,2]. To date, many studies with respect to Zn–Sb based alloys such as phase diagram [3,4], physical properties [5,6] and microstructures [7] have been conducted, but little attention has been paid to the effects of phases on the thermoelectric properties.

Recent works in our group reveal that an addition of Ag/Cu or their compounds with determined concentration in the p-type Bi–Te based alloys can greatly improve thermoelectric performance [8–10], because one of the key points is that there are precipitated metallic phases and possible existence of nanostructures that can reduce lattice thermal conductivities. On one hand, Zn–Sb based alloys are a kind of materials with higher level of atomic disorder and hole concentration, discovered disorder in β-Zn_4Sb_3 manifests in the framework Zn position, which displays a considerable occupational deficiency (0.89–0.90) and in the occurrence of three weakly occupied (by around 0.06) general positions representing interstitial Zn atoms [7]. Therefore, unlike those in the Bi–Te based alloys, only limited doping effect can be expected. On the other hand, however, ZnSb is also known as a thermoelectric (TE) material with larger Seebeck coefficients and higher thermal conductivities than typical semiconductor β-Zn_4Sb_3 does [11–13], if a foreign element is doped into the Zn–Sb based alloys, the effects of formed ZnSb and other precipitated metallic phases on the

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modulation of transport properties should be very important. Considering the fact that elements Cd and In have more valence electrons than Cu and Ag, it is presumed that an incorporation of Cu in the Zn–Sb based alloys can produce more hole concentration, which may effectively optimize the carrier concentration. In addition, an atomic radius of Cu (1.57×10^{-10} m) is smaller than those of Cd (1.71×10^{-10} m) and In (2.0×10^{-10} m) [14], Cu could readily interstitially occupy the gaps in the Zn–Sb lattice, which enhances the lattice distortion and reduces the lattice thermal conductivity. Therefore, an addition of Cu in the Zn_4Sb_3 based alloys could be of great significance to the improvement of TE properties.

In the present work, Cu-added Zn–Sb based alloys with multi-phase equilibrium were prepared and their microstructures and TE properties were evaluated.

2. Experimental

Polycrystalline samples were prepared according to the formula $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) by melting the mixtures composed of high purity (5 N) elements Zn, Sb and Cu in evacuated quartz tubes at 1323 K for 10 h. During melting 30-s rocking every 1 h was conducted to ensure that the composition was homogenous without segregation. After quenching in water the ingots were ball-milled for 5 h in stainless steel bowls with a rotation rate of 350 rpm. The sintering of the powders was carried out with spark plasma sintering apparatus (SPS-1030) using a pre-designed sintering program at a pressure of 40 MPa and 723 K. In order to avoid Zn evaporation from the crystals during sintering [15], a relatively rapid sintering process was recommended with the heating and holding time each of only 5 min. The subsequent heat treatment was conducted for the compacts in vacuum at 453 K for 10 h to ensure homogeneity and to eliminate the internal stress as much as possible. The densities of the samples, measured using an Archimedes method, are in a range from 6.09×10^3 to 6.23×10^3 kg/m^3. Finally, each sample was cut into 3 mm slices measuring 2.5 mm×13 mm from the heat treated compacts with the size of ϕ 20 mm×2.5 mm for property measurements.

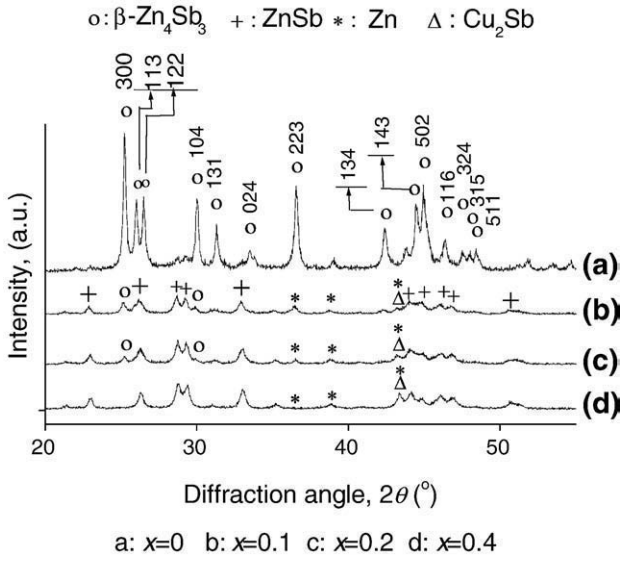

Fig. 1 – X-ray diffraction patterns of the Cu-added $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) alloys.

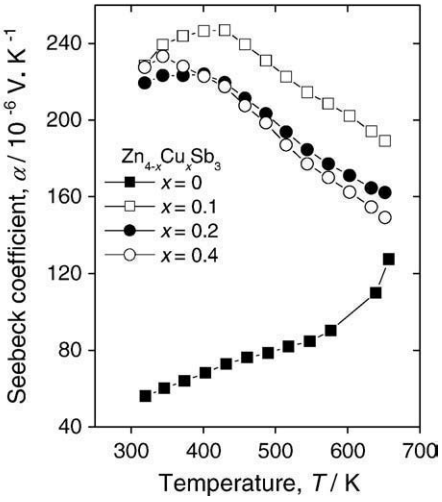

Fig. 2 – The relationship between temperature and Seebeck coefficients for different $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) alloys prepared by spark plasma sintering.

The phase structures were investigated by X-ray diffraction (XRD)with a Rigaku D/MAX-2550P diffractometer using Cu Ka radiation (λ=0.15406 nm), using a scan rate of 4° min^{-1} to record the patterns in the 2θ range from 10 to 100°. Rietveld analyses were performed to determine the atomic incorporation in the Zn–Sb sublattice. The Seebeck coefficients (α) and electrical conductivities (σ) were measured using an apparatus (ULVAC ZEM-2) in a helium atmosphere. Thermal diffusivities were measured by a laser flash method (TC-7000H), and thermal conductivities were calculated from the values of density, specific heat and thermal diffusivity. The Hall coefficients for different samples were measured using an apparatus (HT-648) at 318 K, and the carrier concentrations and mobility were determined using measured electrical conductivities and Hall coefficients.

3. Results and Discussion

3.1. *Microstructures*

Fig. 1 is the XRD patterns of the Cu-added Zn–Sb based (x=0–0.4) samples, indicating that there is a great difference between the profiles for the undoped and Cu-added alloys. The alloy without Cu addition is a β-Zn_4Sb_3 single phase (JCPDS 89-1969) [16] with high peak intensities in the main crystal planes, whereas Cu-added alloys shows only weakened peaks, implying that the grain growth is greatly suppressed after Cu addition. The Cu-added alloys are of structures with multi-phase equilibrium, the structures including a major phase ZnSb (JCPDS 65-2408) [16], small quantities of β-Zn_4Sb_3, Cu_2Sb (JCPDS 65-2815) [16] and remnant Zn (JCPDS 65-5973) [16]. The β-Zn_4Sb_3 phase only occurs in the samples with low content of Cu ($x\leq0.2$), it

Table 1 – The carrier concentrations and Hall mobility obtained near 318 K for the Cu-added Zn–Sb based alloys $Zn_{4-x}Cu_xSb_3$ (x=0–0.4).

Samples with x	Carrier concentrations (cm^{-3}) near 318 K	Hall mobility (cm^2/Vs) near 318 K
0	8.87×10^{19}	67.4
0.1	3.12×10^{19}	4.93
0.2	3.76×10^{19}	9.70
0.4	4.12×10^{19}	9.48

disappears at x=0.4, the peak intensity of Cu_2Sb tends to increase with the starting Cu content, suggesting that the element Cu could not totally dissolve into the Zn–Sb alloy. After close Rietveld analysis to the specimens, we did not find any incorporation of element Cu into the Zn–Sb sublattice, which is inconsistent with the previous expectation, indicating that most Cu atoms were formed in Cu_2Sb compound. The peak intensities of remnant Zn become weaker with Cu content increasing.

3.2. *Thermoelectric Properties*

After Cu addition into the Zn–Sb based alloys, the α values are significantly increased (Fig. 2), and the maximum α value is 246.9 (μV/K) for x=0.1 at 430 K, much higher than that of the β-Zn_4Sb_3 with the maximum α value of 127.5 (μV/K). There are two factors that influence the Seebeck coefficient, scatter factor s and carrier concentration n, according to the expression: $\alpha=\frac{\kappa_B}{e}\left[s+\frac{5}{2}+ln\frac{2(2\pi m^*\kappa_B T)^{\frac{3}{2}}}{nh^3}\right]$ [17]. We calculated carrier concentrations and mobility using measured Hall coefficients for different samples near 318 K, and observed a markedly decreased Hall mobility and carrier concentration for the Cu-added alloys, as shown in Table 1. Since there are several phases in the Cu-added alloys, complex structures can cause an enhancement of carrier scattering, leading to the increase in scattering factor s. We therefore consider that in the present work both the increased scatter factor s and carrier concentration n controls the α values. With the increasing of the Cu_2Sb content the Seebeck coefficient and electrical resistivity tend to decrease, we presume that this metallic phase is of significance to the contribution of free carrier concentration. Contrary to the dependence of Seebeck coefficient, we observed a noticeable decrease of the electrical conductivities (σ) at low temperatures, as shown in Fig. 3. Similarly, this decrease of σ is also attributed to the substantial reduction in mobility μ and n (Table 1). Because the quantity of ZnSb phase takes a large proportion in the present alloys, this major phase was reported to have a higher electrical resistivity (1.1×10^{-4} Ω m), Seebeck coefficient (196 μV/K) and much lower hole concentration (6.3×10^{-24} m^{-3}) at room temperature (R.T.) than β-Zn_4Sb_3 (2.2×10^{-5} Ω m, 115 μV/K and 6.8×10^{-25} m^{-3}, respectively) does [13], therefore, the ZnSb phase plays an important role in controlling the transport data in the present materials.

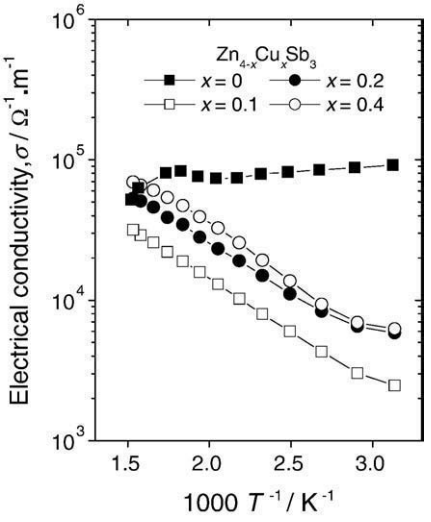

Fig. 3 – The dependence of electrical conductivities on temperature for different $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) alloys prepared by spark plasma sintering.

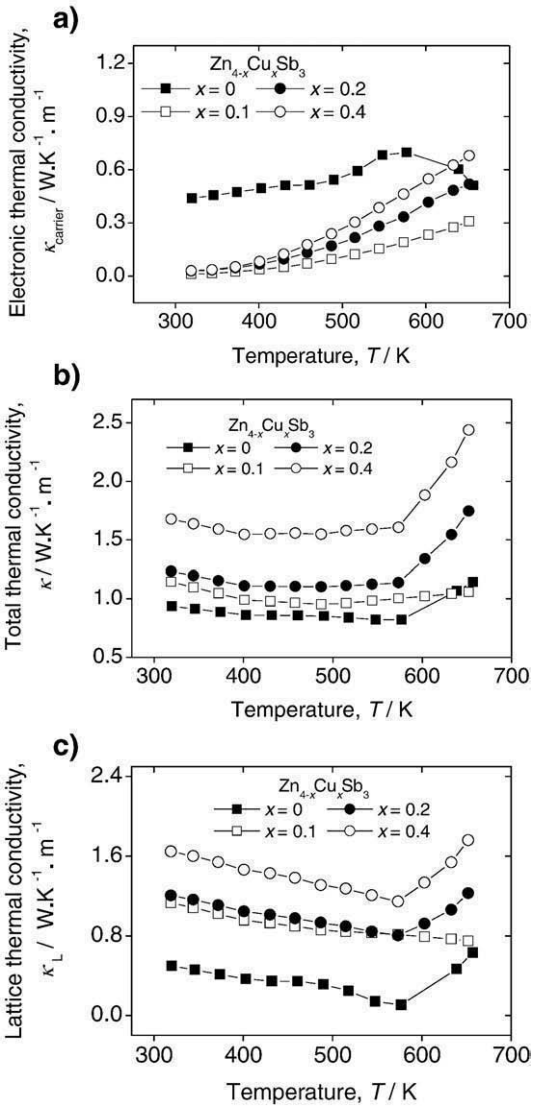

Fig. 4 – The temperature dependence of thermal conductivities for different $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) alloys prepared by spark plasma sintering, (a) $\kappa_{carrier}$–T, (b) κ–T, (c) κ_L–T.

The temperature dependences of thermal conductivities (κ), electronic component ($\kappa_{carrier}$) and lattice contribution (κ_L)

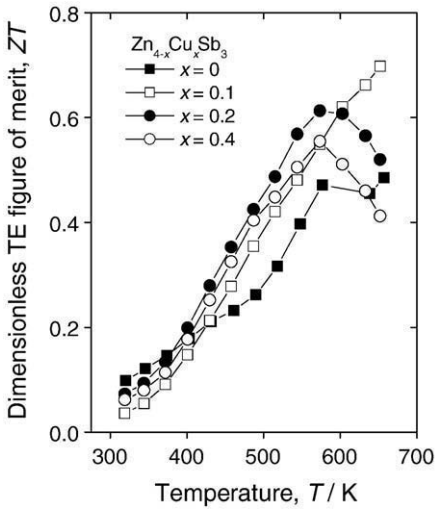

Fig. 5 – The temperature dependence of dimensionless TE figure of merit *ZT* for different $Zn_{4-x}Cu_xSb_3$ (x=0–0.4) alloys.

are shown in Fig. 4. The $\kappa_{carrier}$ values are estimated from the Wiedmann–Franz law as $\kappa_{carrier}=LT\sigma$ (Fig. 4a), where L is taken to be 1.5×10^{-8} V^2K^{-2} [18], T is absolute temperature. The κ values enhance with starting Cu content, and keep relatively constant below 574 K (Fig. 4b). At x=0.1 the κ values are very close to those for the undoped β-Zn_4Sb_3 over the entire temperature range, and are 1.14 (W/mK) and 1.05 (W/mK) at R. T. and 654 K, respectively. The alloy at x=0.4 has higher κ values than others for the corresponding temperatures, but still remain similar temperature dependence. The Cu-contained alloys have higher κ_L values than β-Zn_4Sb_3 does (Fig. 4c), the reason is that the κ_L values of ZnSb are much higher than those of β-Zn_4Sb_3 [13]. A typical data can confirm this point, for example, the κ_L value of ZnSb is 2.26 (W/mK) at R.T., whereas that of β-Zn_4Sb_3 is 0.74 (W/mK) [13]. The lattice thermal conductivities for the Cu-added alloys enhance with the Cu_2Sb content, which might mainly be ascribed to the higher κ_L values of the ZnSb itself. A rapid enhancement with temperature for the κ_L values above 574 K might be resulted from an ambipolar contribution.

ZT is defined as $ZT=\alpha^2\sigma T/\kappa$, the resulting *ZT*s are shown in Fig. 5. There is a big improvement in *ZT* over present β-Zn_4Sb_3, the maximum *ZT* value of 0.70 is achieved for the Cu-added alloys with x=0.1 at 654 K, about 0.22 higher than that of the present β-Zn_4Sb_3 at the corresponding temperature. Therefore, the TE properties of Zn–Sb based alloys can simply be improved by adding a small amount of cheap Cu element, and the second phase Cu_2Sb with proper concentration is of significance to the improvement of the thermoelectric performance for the Zn–Sb based alloys.

4. Conclusion

After addition of Cu into the Zn–Sb based alloys, multi-phase structures can be obtained, the major phase ZnSb plays an important role in determining the transport properties, the second phase Cu_2Sb, which increases with starting Cu content, is of significance to the improvement of the TE performance. The maximum *ZT* value of 0.70 is achieved for the alloy with a certain Cu concentration at 654 K, about 0.22 higher than that of the present β-Zn_4Sb_3 at the corresponding temperature.

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